

Supporting information for:

Femtosecond and Attosecond Electron
Transfer Dynamics in PCPDTBT:PCBM Bulk
Heterojunctions

F. O. L. Johansson,[†] M. Ivanović,[‡] S. Svanström,[†] U. B. Cappel,^{†,¶} H. Peisert,[‡] T.
Chassé,[‡] and A. Lindblad*,[†]

[†]*Department of Physics and Astronomy, Molecular and Condensed Matter Physics,
Uppsala University, Box 516, SE-75120 Uppsala, Sweden*

[‡]*Institut für Physikalische und Theoretische Chemie, Universität Tübingen, Auf der
Morgenstelle 18, D-72076 Tübingen, Germany*

[¶]*Present adress: Division of Applied Physical Chemistry, Department of Chemistry, KTH
- Royal Institute of Technology, SE-100 44 Stockholm, Sweden*

S1 Energy level alignment with UPS

The energy level alignment of PCPDTBT and PCBM blends are determined from the relative position of core levels in XPS. The energy level alignment of PCBM and PCPDTBT to ITO is determined from the high and low kinetic energy cut-offs in UPS.

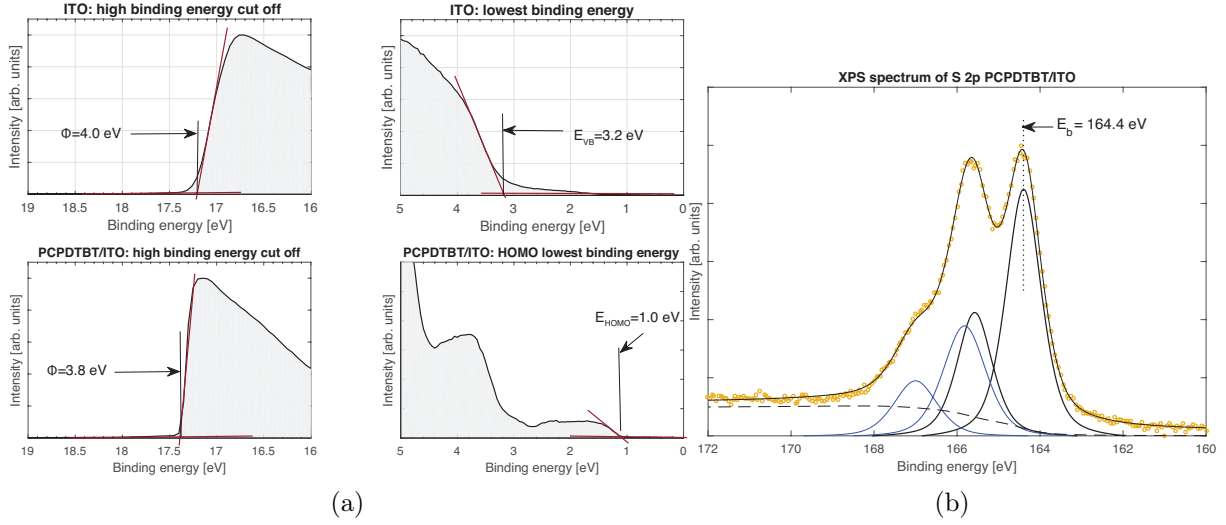


Figure S1: Photoemission spectra of PCPDTBT on ITO. a) UPS spectra with zoom into the HOMO/VB region (right) and the high binding energy cutoff (left). b) XPS spectrum of the S 2p core level, the vertical line indicates 164.5 eV binding energy position used for the (indirect) determination of the HOMO onset and the vacuum level.

The numbers indicated in the spectra are such that E_{HOMO} gives the ionization potential of the top of the HOMO (E_{HOMO}) relative to the vacuum level together with the work function Φ : $IP = E_{HOMO} + \Phi$. For ITO the E_{VB} is the top of the valence band relative to the Fermi level, and $IP = E_{VB} + \Phi$. The ionization potentials are indicated in Fig. 1, in the main text, as IP2 and IP3.

The quantities to be determined in the energy level diagram presented in that figure is the work function Φ and the ionization potential of the material relative to the vacuum level. The two quantities are related to the photon energy $\hbar\omega$, electron binding energy E_b and the observed kinetic energy of the electron E_{kin} by Einstein's relation for the photoelectric effect:

$$E_{kin} = \hbar\omega - E_b + \Phi \quad (1)$$

Thus, using a fixed photon energy in the experiment, *e.g.* 21.2 eV for a He I discharge lamp, the work function Φ can be determined from the position of the low kinetic energy cut-off with respect to the Fermi level. The position of the HOMO (E_{HOMO}) is determined from the low binding energy onset. The ionization potential IP of the polymer corresponds to, as above $IP = \Phi + E_{\text{HOMO}}$.

Pristine PCPDTBT and PCBM films were prepared on ITO. The basic electronic parameters, as obtained from UPS measurements, are summarized in Table S1. The corresponding spectra can be found in Figures S2 and S1. To illustrate further the positions of the LUMO levels – important for charge transfer of excited states – we use the transport gap of PCBM from the literature.^{S1,S2} Due to the lack of inverse photoemission data for PCPDTBT the optical gap (E_g^{opt}) is used as an estimate of the LUMO position. Neglecting excitonic effects in the case of PCPDTBT will result in smaller values of the gap and thus of a lowering of the LUMO position. Nevertheless, the LUMO position of PCPDTBT estimated in this manner lies still well above the LUMO position of PCBM.

Table S1: Measured values for ionization potential (IP), work function (Φ). The values are the same for mixing ratios 1:1, 1:2 and 1:3, as determined from UPS. For the polymer the optical band gap was determined by UV/Vis spectroscopy.

Quantity	PCPDTBT	PCBM
IP [eV]	4.8	6.1
Φ [eV]	4.4	4.3
Band gap [eV]	1.45	2.3 [¶]

^{||} Measured by UV/Vis spectroscopy.

[¶] Transport gap from Refs. S1 and S2.

In order to study the energy level alignment in *blends*, we determine the relative energy of representative core levels for the two materials to the HOMO and vacuum levels. The S 2p core level binding energy of the thiophene component of PCPDTBT relative to the HOMO onset was determined to be 163.4 eV, relative to the vacuum level (E_V) we add the ionization potential to obtain 168.2 eV. In the case of PCBM the peak from doubly bonded oxygen at high binding energy in the O 1s spectrum was used (at lower binding energy, a peak from

the oxygen attached to the methyl group can be found).^{S3} For the 1:1 blend, a third peak at even lower binding energy is present at 530.4 eV, lying between the expected values of oxygen in SnO and SnO₂,^{S4} as expected for oxygen in the ITO substrate. We determine for the pristine film 531.8 eV energy difference between O 1s and the HOMO, giving 537.9 eV referenced to the vacuum level. The corresponding spectra are shown in Figures S2 and S1. Thus, assuming a vacuum level alignment regime in a blend between PCPDTBT and PCBM, the energetic distance between O 1s and S 2p core levels, both referenced to E_V , is 369.7 eV.

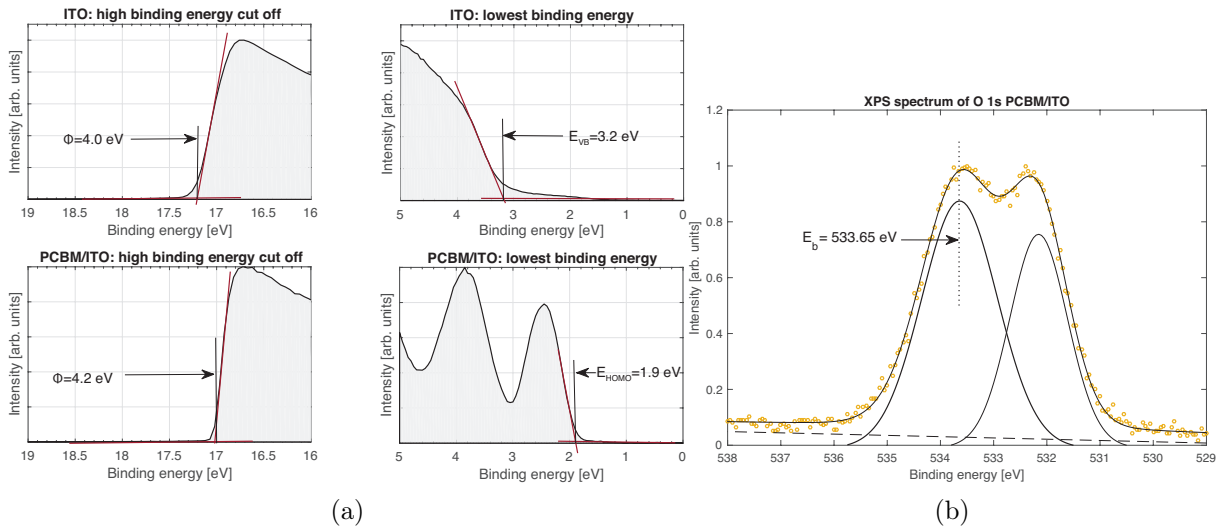


Figure S2: Photoemission spectra of ITO and PCBM on ITO. a) UPS spectra with zoom into the HOMO/VB region (right) and the high binding energy cutoff (left) which allows the determination of the work function. b) XPS spectrum of the O 1s core level, the vertical line indicate 533.65 eV binding energy used for the (indirect) determination of the HOMO onset and the vacuum level.

The numbers indicated in the spectra are such that IP gives the ionization potential of the top of the HOMO (E_{HOMO}) relative to the vacuum level: $IP = E_{HOMO} + \Phi$. This ionization potential is indicated in Fig. 1 (main text) as IP2 and IP3 respectively.

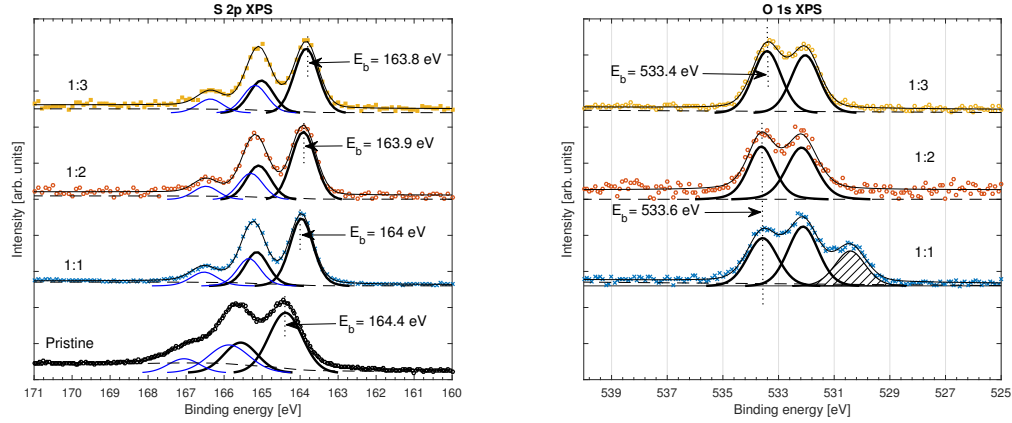


Figure S3: XPS detail spectra of thin films of pristine polymer and blends used for (indirect) determination of the energy level alignment between PDPDTBT and PCBM. a) S 2p region (PCPDTBT) b) O1s region (PCBM).

Fig. S3 is of the S 2p and O 1s core levels XPS spectra of pristine polymer and blends obtained with Al $K\alpha$ X-rays. The binding energies for the components are used for the determination of the parameters (Tab. S1 in the main text) for the energy level alignment diagram in Fig. 1 (main text). The hatched component of the O 1s spectrum with binding energy 530.4 eV falls between the binding energy values for O 1s in SnO and SnO₂^{S4} and in the interval of obtained values for the oxygen core level binding energy in indium doped tin oxide prepared with various methods (530.0 eV^{S5} to 530.8 eV^{S6}).

S2 HAXPES

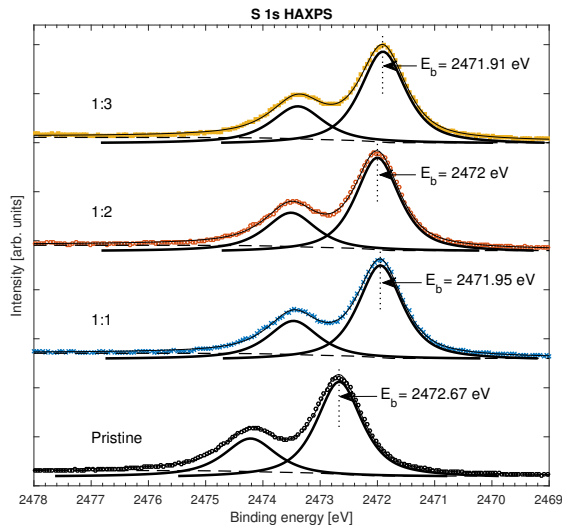


Figure S4: Sulfur 1s core level photoelectron spectra of pristine polymer and PCBM blends. The least squares fit results are included: at low binding energy the CPDT sulfur’s binding energy is included in the figure, the higher binding energy component is that of BT.

The energy positions and area ratios of the sulfur 1 s core level spectra for the different blends (Fig. S4) have been obtained with least squares fits using Voigt functions for the two components and a Shirley background. The results of those fits, where the Gaussian width of the two components have been set equal to the instrumental broadening (as given by a fit to the Au 4f core level line taken without changing instrumental settings) with the two Lorentzian lifetime broadenings free, are given in Table S2.

If two independent Lorentzians are used the ratio between the two components are close to 2 – as expected from the stoichiometry of the polymer. This using Lorentzian widths of 750 meV and 900 meV for the cyclopentadithiophene (CPDT) and benzothiadiazole (BT) sulfurs respectively.

We have tried to fit the data in additional ways with: free Gaussians and Lorentzians for each component; Gaussians from the instrumental resolution together with Lorentzians free but equal in magnitude for the two components, and Gaussians and Lorentzians free but equal in respective magnitude for the two components. They give reasonable fits to the data

Table S2: Position of the different components for the S 1s spectra taken at 6300 eV (3rd order of 2100 eV) for the different blends. All positions are calibrated to Au 4f. Average of first peak position for PCPB, C and D is 2471.95 ± 0.05 eV.

Sample	CPDT	BT	Area ratio
PCPA2	2472.67	2474.22	1.98
PCPB	2471.95	2473.46	2.04
PCPC	2472.00	2473.51	1.85
PCPD	2471.91	2473.39	1.92

but with the ratio between the components being between 2.4 and 2.6, *i.e.* exaggerating the CPDT content.

S3 S KLL Auger electron spectra

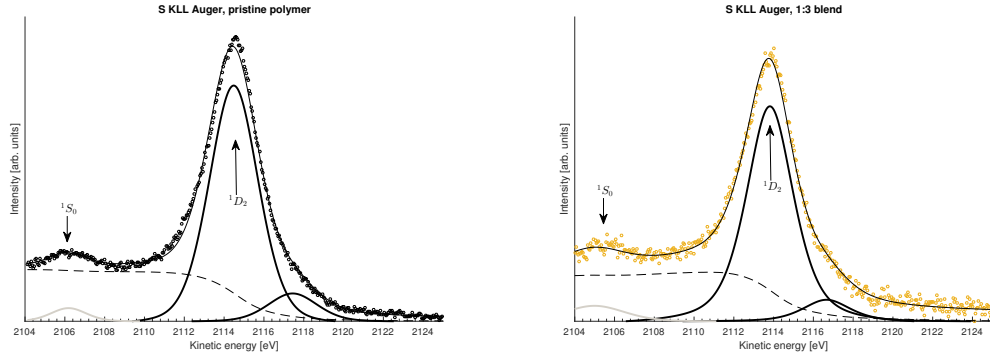


Figure S5: S KLL Auger spectra taken with an excitation energy of $\hbar\omega = 5000$ eV on pristine polymer and the most dilute blend. The main lines are designated as used in the text.

S3.1 Overview spectra

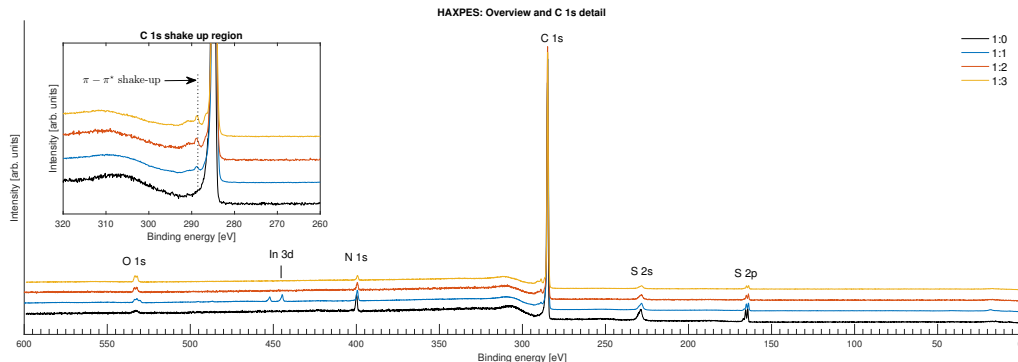


Figure S6: Overview spectra of pristine polymer and blends. The presence of In 3d (binding energy 444.6 eV) from the ITO for the 1:1 blend show that this sample is somewhat thinner than the other blends. Inset show the shake-up region in the C 1s core level spectra.

Table S3: Binding energies obtained from the overview spectra. All energies are given in eV.

Level	Pristine	1:1	1:2	1:3
S 2p _{3/2} CPDT	164.4	163.9	163.9	163.8
S 2p _{3/2}	165.8	165.4	165.4	165.3
S 2s CPDT	228.7	228.3	228.3	228.2
S 2s	230.3	229.8	229.7	229.9
C 1s	285.0	284.7	284.8	284.7
$\pi - \pi^*$		288.8	288.9	288.8
N 1s	399.9	399.4	399.5	399.4
O 1s ITO		530.3		
O 1s	(532.5)	532.1	532.2	532.1
	(534.0)	533.5	533.6	533.4

In Table S3 binding energies of the overview spectra in Fig. S6 are given. For the sulfur 2p core levels the spectrum consists of two spin-orbit multiplets, the spin-orbit component with the lowest binding energy are given in the table. The shake-up present in the C 1s spectrum of the PCBM blends is designated $\pi - \pi^*$ (discussed in the main text). The parenthesis around the O 1s binding energies for the pristine polymer indicate that these are from trace contaminants on the surface.

S3.2 Resonant Auger spectra

The photon energies where the resonant Auger spectra in the S KLL electron kinetic energy region were taken are presented in in Tab. S4. The spectra follows below. The 1:1 blend is discussed in the main text.

Table S4: Designated points together with photon energies, in eV.

	Pristine	1:2	1:3
T1	2472.5	2472.7	2472.6
B1	2473.3	2473.5	2473.4
T2	2474.3	1474.5	1474.4
B2	2475.7	2475.9	2475.8
P1	2477.2	2477.4	2477.3
After resonance	2487.2	2487.4	2487.3

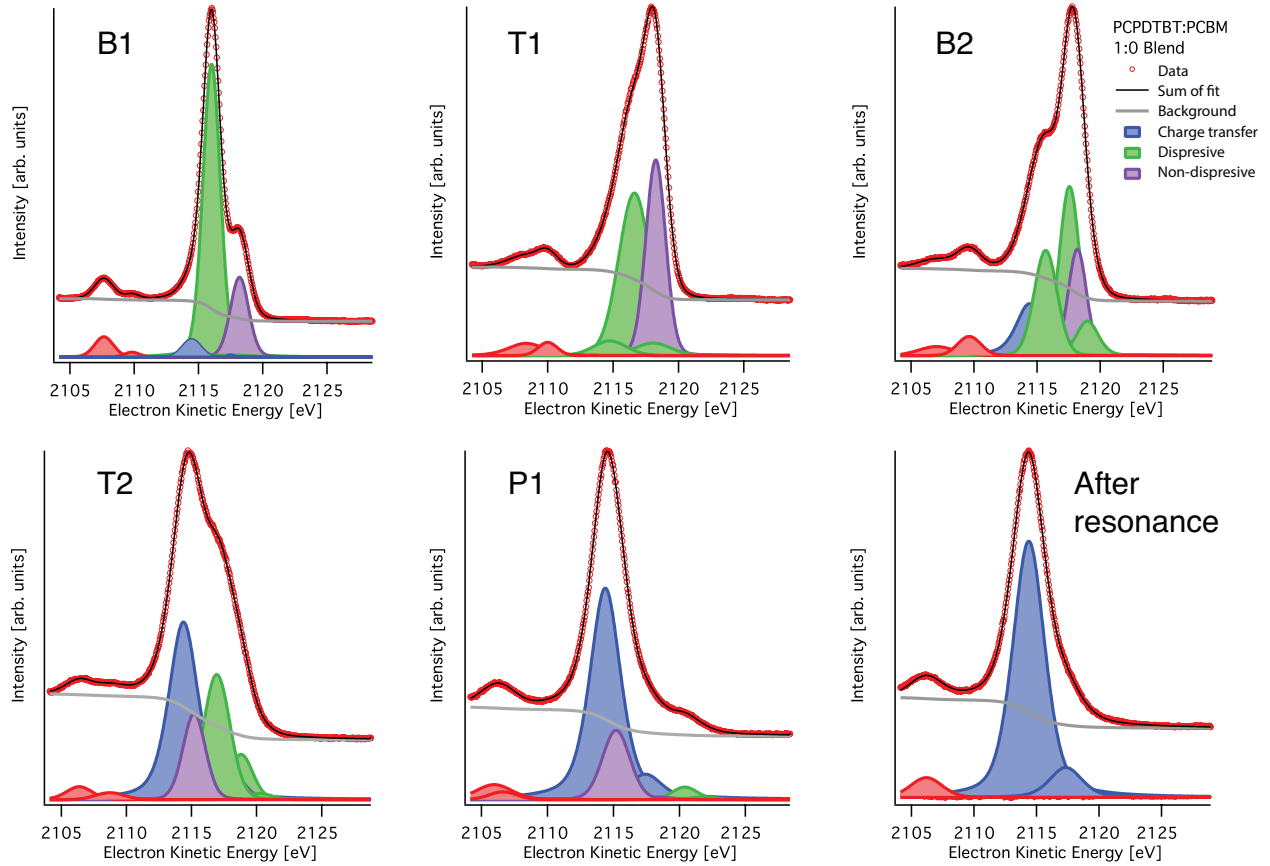


Figure S7: Resonant Auger spectra of the pristine polymer sample.

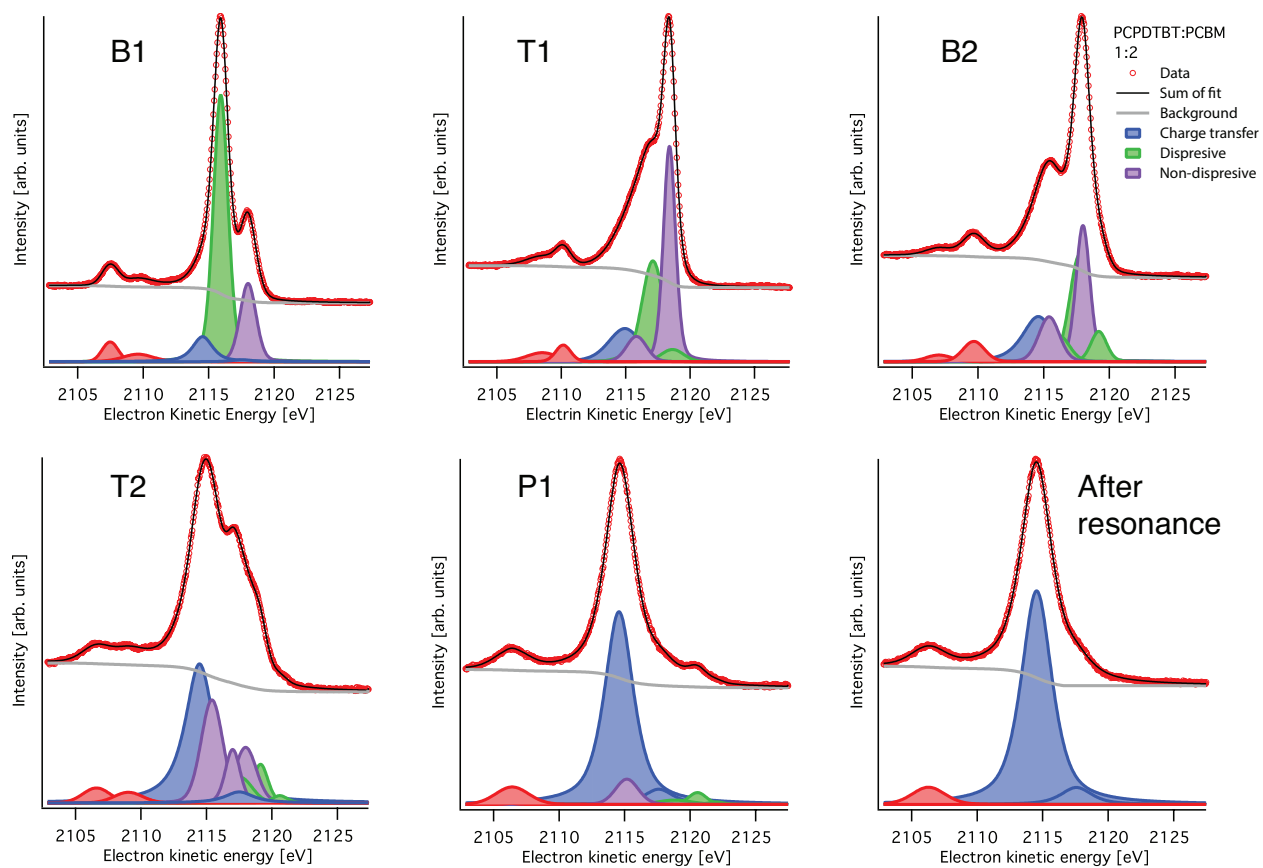


Figure S8: Resonant Auger spectra of the 1:2 polymer blend sample.

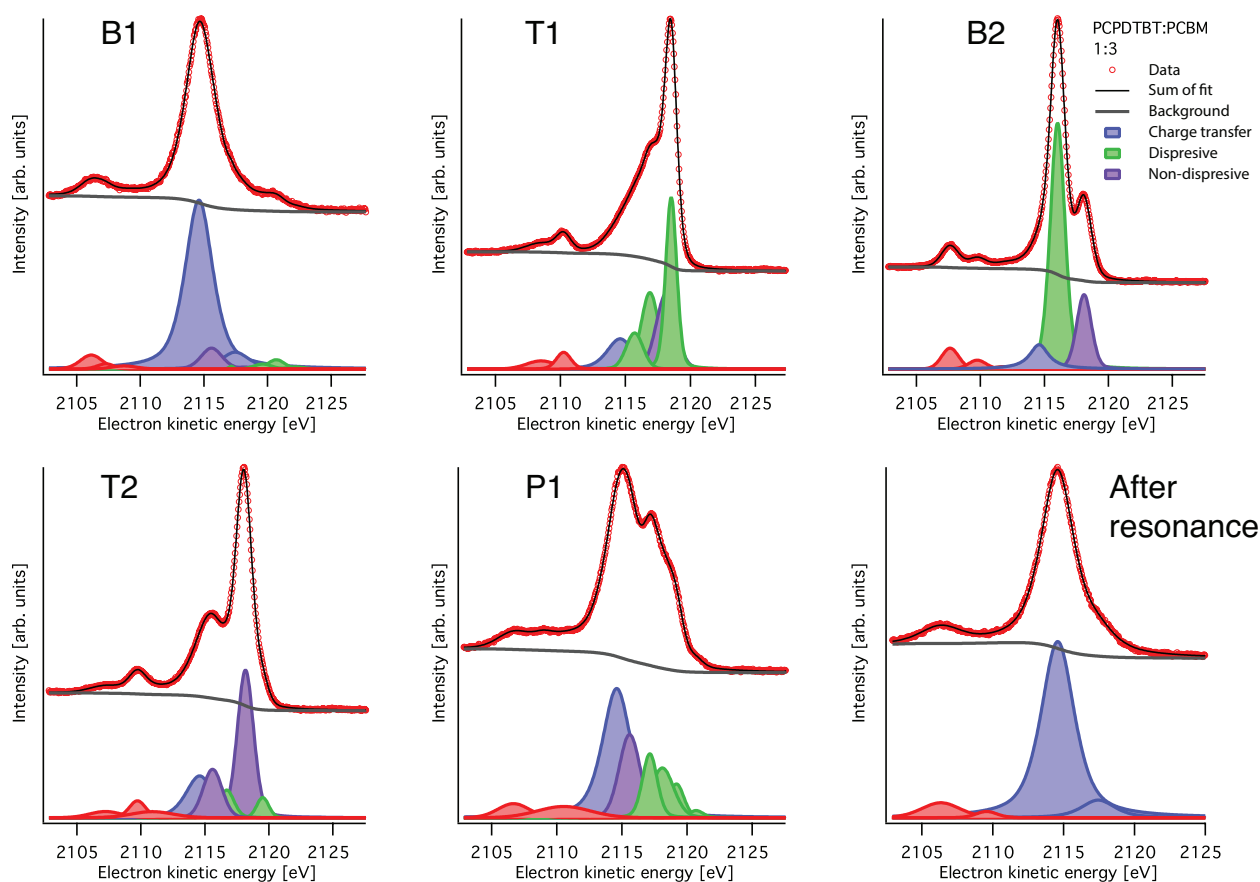


Figure S9: Resonant Auger spectra of the 1:3 polymer blend sample.

References

- (S1) Bao, Q.; Sandberg, O.; Dagnelund, D.; Sandén, S.; Braun, S.; Aarnio, H.; Liu, X.; Chen, W. M.; Österbacka, R.; Fahlman, M. Trap-Assisted Recombination Via Integer Charge Transfer States in Organic Bulk Heterojunction Photovoltaics. *Adv. Func. Mat.* **2014**, *24*, 6309–6316.
- (S2) Guan, Z.-L.; Kim, J. B.; Wang, H.; Jaye, C.; Fischer, D. A.; Loo, Y.-L.; Kahn, A. Direct Determination of the Electronic Structure of the Poly (3-Hexylthiophene): Phenyl-[6, 6]-C₆₁ Butyric Acid Methyl Ester Blend. *Org. Electr.* **2010**, *11*, 1779–1785.
- (S3) Richter, M. H.; Friedrich, D.; Schmeißer, D. Valence and Conduction Band States of

PCBM As Probed by Photoelectron Spectroscopy at Resonant Excitation. *BioNanoSci.* **2012**, *2*, 59–65.

- (S4) Fondell, M.; Gorgoi, M.; Boman, M.; Lindblad, A. An HAXPES Study of Sn, SnS, SnO and SnO₂. *J. Electron Spectrosc.* **2014**, *195*, 195 – 199.
- (S5) Fan, J. C. C.; Goodenough, J. B. X-Ray Photoemission Spectroscopy Studies of Sn-Doped Indium-Oxide Films. *J. Appl. Phys.* **1977**, *48*, 3524–3531.
- (S6) Ishida, T.; Kobayashi, H.; Nakato, Y. Structures and Properties of Electron-Beam-Evaporated Indium Tin Oxide Films As Studied by X-Ray Photoelectron Spectroscopy and Work-Function Measurements. *J. Appl. Phys.* **1993**, *73*, 4344–4350.